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(19)

(54) PIGMENTED PAINT

(71) We, TH. GOLDSCHMIDT A.G., a German Body Corporate, of 43 Essen, Goldschmidtstrasse 100, Germany and EMIL G.V. HÖVELING, a German Body Corporate, of 2102 Hamburg 93, Am Alten Schachthof 16, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pigmented paints based on siloxane resins and polymers of methacrylic acid esters especially useful as a water-repellent facade-protecting paint.

The paint of this invention can be used for rendering building material of a mineral nature water-repellent.

It is known from German Auslegeschrift 1,671,280 that mixtures of siloxane resins and polymethacrylic acid methyl esters can be employed as colourless impregnating agents for building materials and have a water-repellent effect. Such impregnating agents penetrate deeply into the building material and do not leave a visible film on the surface. Their water-repellent action is associated with increasing the interfacial tension of the water. The solids content of these impregnating agents in organic solvents is relatively low and is only approx. 3 to 8%, depending on the absorbency of the building material. Furthermore, a high proportion of aromatic solvents is required to achieve adequate compatibility of the siloxane resin with the copolymer.

In contrast to colourless impregnating agents, the optical effect of pigmented paints is important, the stability of the colour shade, and the gloss retention, being particularly important. A certain minimum pigment volume concentration is normally required to achieve adequate opacity and weathering-resistant properties.

The present invention provides a pigmented paint containing a polymer of a methacrylic acid ester and a siloxane resin having units of the general formula

$$R^1_a - Si - (OR^2)_b \quad O\left[\frac{4-(a+b)}{2}\right]$$

wherein R^1 is a methyl and/or phenyl radical, R^2 is an alkyl radical with 1 to 4 carbon atoms, a has a value of 0.5 to 1.8 and b has a value of 0.2 to 2.5, preferably 0.3 to 1.2, the weight of siloxane resin being 10—50% by weight of the polymer.

The choice of the indices a and b in the ranges indicated ensures that the siloxane resin is of relatively low molecular weight.

The solixane resins used in the invention are known and their production is described, for example, in German Patent Specification No. 2,020,224.

The hydrolysis and subsequent condensation of the OR^2 groups present in the siloxane resin contained in the paints of the invention takes place under the influence of atmospheric moisture, even at room temperature. The condensation of these compounds is accelerated by catalysts, for example tin catalysts, especially dialkyl - diacyl - tin compounds. Dibutyl-tin dilaurate is a particularly suitable catalyst. The organo-tin catalysts have the advantage that they are also compatible with the methacrylic acid polymer. Further catalysts which can be used in the paints and additional comments on the catalysis are to be found in "Chemie und Technologie der Silicone" by Walter Noll, Verlag Chemie GmbH (1968) at page 340.

The paint according to the invention therefore preferably contains catalysts which accelerate the hydrolysis and condensation, and in particular, the above-mentioned organo-tin catalysts.

Siloxane resins in which the group R^1 represents a mixture of methyl and phenyl radicals are preferably used because they are readily compatible with the polymer component. Preferably, 20 to 80 mol% of the radicals R^1 are phenyl radicals.

The siloxane resins contained in the paint of the invention exhibit good compatibility with the polymer of the methacrylic acid ester. The particular polymer of the methacrylic acid ester used is not critical and examples of suitable polymers are those produced by polymerisation of esters of methacrylic acid or copolymerisation of esters of methacrylic acid and a copolymerisable monomer e.g. an ester of acrylic acid. The esters of methacrylic acid, and of acrylic acid, when they are used, will normally be methyl, ethyl, propyl, isobutyl or butyl esters. Esters where the alkyl group has at least 3 carbon atoms are preferred and at least the predominant proportion of the polymer (e.g. at least 70 molar percent) should preferably be the n-butyl ester or isobutyl ester of methacrylic acid, because of the good solubility in benzene of the resulting polymer.

The good compatibility of the low molecular weight siloxane resins with the polymer results in the uniform distribution of the siloxane molecules in the paint film so that even at a low concentration of the siloxane resin, relative to polymer, a water-repellent effect is achieved. Preferably, the paints contain about 10% by weight of siloxane resin, relative to polymer.

The paints of the invention generally have a relatively high binder content and a low solvent content. The relatively high binder content is advantageous for weathering resistance and covering power. The high concentration, coupled with the use of an aliphatic solvent, is furthermore advantageous because this facilitates the practical use of the product by roller or brush application, even in cases of overpainting. It is particularly advantageous to use copolymers which are soluble in aliphatic solvents in the mixture of pigmented paints.

The table which follows shows typical recipes for paints according to the invention and comparative paint compositions containing smaller amounts of siloxane resin. The water repellency exhibited after two days is also shown. All numerical data in the table are percentages by weight. The siloxane resins used are designated by the figures I, II and III in the Table.

Siloxane resin I has units of the following structure:

$$(C_6H_5)_{0.25}\,(CH_3)_{0.75}\text{—}Si\text{—}(OCH_3)_{0.93}$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad O_{1.935}$$

Siloxane resin II has units of the following structure:

$$(C_6H_5)_{0.8}\,(CH_3)_{0.2}\text{—}Si\text{—}(OC_2H_5)_{1.2}$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad O_{0.9}$$

Siloxane resin III has units of the following structure:

$$(CH_3)_{1.13}\text{—}Si\text{—}(OC_4H_9)_{0.34}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad O_{1.25}$$

TABLE

	Comparison		Examples					
	1	2	1	2	3	4	5	6
1. Siloxane resin I	0.50	1.00	2.00	3.00	4.00	5.00	–	–
2. Siloxane resin II	–	–	–	–	–	–	3.00	–
3. Siloxane resin III	–	–	–	–	–	–	–	3.00
4. Catalyst: organic tin compound	0.05	0.05	0.05	0.10	0.10	0.10	0.10	0.10
5. Polymethacrylic acid ester*	14.50	14.00	13.00	12.00	11.00	10.00	12.00	12.00
6. Chlorinated paraffin (63% chlorine)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
7. Titanium dioxide	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
8. Micronised mica	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
9. Aluminium stearate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
10. Aliphatic solvent	45.95	45.95	45.95	45.90	45.90	45.90	45.90	45.90
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Water repellency after 2 days:	None	Slight	Good	Very good	Very good	Very good	Very good	Very good

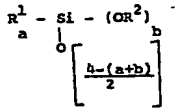
* 30 mole percent methyl ester and 70 mole percent n-butyl ester.

It is found that using the paints according to the invention, a surprisingly good water-repellent action is achieved even when the siloxane resin content is as low as 2 to 5% by weight of the paint. The comparison mixtures, not in accordance with the invention, are distinctly poorer.

Compared to conventional paints for facades, the pigmented paint according to the invention has the advantage of high penetrating power and high adhesion, especially to mineral substrates, including those which have been treated beforehand with silicone resins or other non-polar impregnating agents. The treated facades exhibit high water vapour diffusion, low water absorbency and high water repellency in the sense of increasing the interfacial tension. This assists in regulating the water balance, for example, in walls.

WHAT WE CLAIM IS:—

1. A pigmented paint containing a polymer of a methacrylic acid ester and a siloxane resin having units of the general formula



wherein R^1 is a methyl and/or phenyl radical, R^2 is an alkyl radical with 1 to 4 carbon atoms, a has a value of 0.5 to 1.8 and b has a value of 0.2 to 2.5, the weight of siloxane resin being 10—50% by weight of the polymer.

2. A paint according to claim 1, wherein the resin is one in which b is 0.3 to 1.2.

3. A paint according to claim 1 or 2, wherein the amount of siloxane resin is 2 to 5% by weight, based on the weight of the paint.

4. A paint according to any one of the preceding claims, containing a condensation catalyst for the siloxane resin.

5. A paint according to claim 4, wherein the catalyst is an organo-tin compound.

6. A paint according to claim 4 or 5, wherein the catalyst is dibutyl-tin dilaurate.

7. A paint according to any one of the preceding claims, wherein the polymer of a methacrylic acid ester is a copolymer of a methacrylic acid ester and a copolymerisable monomer.

8. A paint according to Claim 7, containing a copolymer of a methacrylic acid ester and an acrylic acid ester.

9. A paint according to any one of the preceding claims, wherein the polymer or copolymer is a polymer or copolymer of an alkyl ester of methacrylic acid where the alkyl group contains 1—4 carbon atoms.

10. A paint according to any one of the preceding claims, wherein the polymer or copolymer is a polymer or copolymer of an alkyl ester of methacrylic acid where the alkyl group contains at least 3 carbon atoms.

11. A paint according to Claim 9, wherein at least 70 molar percent of the polymer or copolymer is a polymer or copolymer of n-butyl or isobutyl methacrylate.

12. A paint according to Claim 1, substantially as hereinbefore described.

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